SYNTHESIS OF CARBON NANOTUBE

AND

THE STUDY OF TRANSFER CHARACTERISTICS OF FET CONFIGURRED CNT DEVICE

Dissertation submitted in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

PHYSICS

By

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Under the Supervision
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ODISHA-769008

2012-2014

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CERTIFICATE

This is to certify that the work in the report entitled "**Synthesis of CNTs by Pyrolysis and fabrication and study of the electrical transport characteristics of FET configured CNT device"** " by Subhasmita Mishra, in partial fulfilment of Master of Science degree in PHYSICS at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best of my knowledge.

Supervised by

Date- 10-05-2014

Place- Rourkela

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DECLARATION

I hereby declare that the project work entitled "**Synthesis of CNTs by Pyrolysis and fabrication and study of the electrical transport characteristics of FET configured CNT device"** submitted to the NIT, Rourkela, is a record of an original work done by me under the guidance of Dr. Pitamber Mahanandia, Faculty Member Department of Physics, NIT, Rourkela. This project work has not been performed on the basis for the award of any Degree or diploma/ associate ship/fellowship and similar project if any.

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ACKNOWLEDGEMENT

I would like to convey my gratitude and sincere thanks to my supervisor **Prof. Pitamber Mahanandia**, Department Of Physics NIT Rourkela, for his constant motivation and support during the course of my project work. I truly appreciate and value his guidance and encouragement from beginning to the end of this thesis.

I wish to express my sincere thanks to **Bamadev Das** M.Tech (R) for his continuous encouragement and supervision of this project work. I am also thankful to all the PhD scholars

Prakash Mahakul and **Kadambinee Sa** for their liberal co-operation and great support in my project work.

I record my sincere thanks to Department of Metallurgical and Material Science and Department of Ceramic Engineering for extending all facilities to carry out the SEM and FESEM.

I express my sincere thanks to all the faculty members of Department of Physics, NIT Rourkela who have made direct or indirect contribution towards the completion of this project. It gives me an enormous pleasure to thank all my friends and all the research scholars of the Dept. of Physics. In particular, I would like to thank my parents for their unconditional love and patience.

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Abstract:

Due to the nanoscale structures of carbon nanotubes with highly appreciable optical, thermal and electrical properties which has lead it into a challenging purpose for many potential applications in the nano channel FET, MOSFET, MISC, biosensors, magnetic storage, memory devices etc. The preparation techniques of CNTs by conventional CVD or ARC plasma Discharge method is substituted by the low cost and easy pyrolysis technique as referred in a paper is used for the preparation of CNTs and the prepared CNT is characterized by XRD, SEM . Then a device using the millimetre long CNT, synthesized by CVD technique, as channel is fabricated in a simple manner and the substrate induced biasing effect has studied by the current -voltage characterization by using the source meter, showing the metallic behaviour of multi walled CNT channel. The change in resistance due to the exposure of fabricated device towards different external factors like LASER beam and the water vapour is observed, which shows the change in surface activity due to the influence of foreign molecules.

CONTENTS

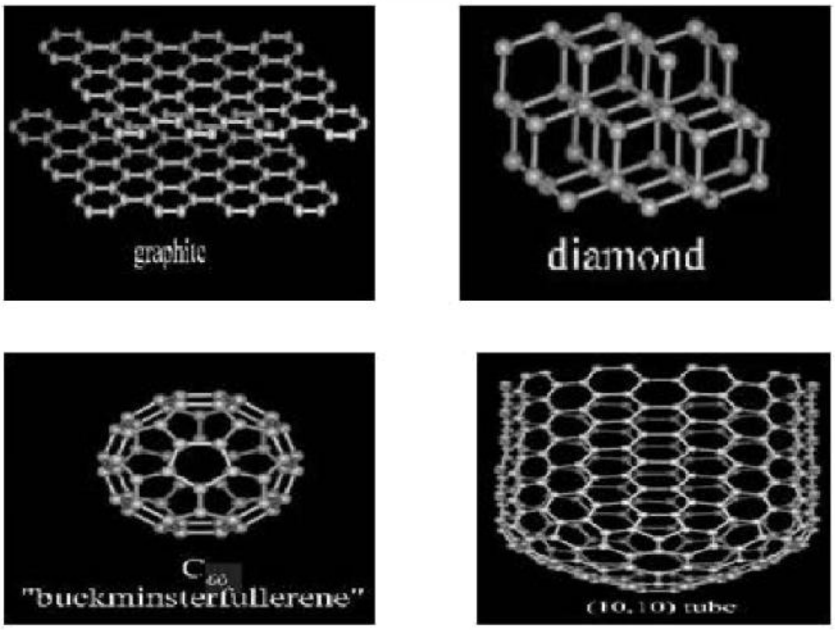
Chapter-I

Introduction

1.1 The Carbon Family and Discovery of Carbon Nanotube:

Until 1980's the carbon was believed to exist only in solid forms as diamond and graphite, known as the carbon allotropes [1] but when in 1985 a group of researchers vaporised a sample of graphite with an intense pulse of LASER and used a stream of helium gas to carry the vaporised graphite into mass spectrometer, which showed a peaks corresponding to molecules composed of 60 carbon atoms. This C-60 clusters were easily formed led the group to repose the new allotropic form of carbon with a spherical structure formed a ball with 32 faces, where 12- carbons in were pentagonal shapes and 20 were hexagonal like a soccer ball. This new allotrope of carbon is known as fullerene or 'the bucky ball', which are inhibitor and the potential block of interstellar space [1-2].

Figure (1),(2),(3),(4) shows the structures of graphene, diamond , fullerene and CNTs respectively[1]



Unique geometrical properties of these new allotropes didn't end with the soccer shaped ball rather lead to the discovery of carbon allotropes in a tubular form well known as carbon nanotube, formed by the rolling of graphene sheet. These having unique physical and chemical properties much efficient for laboratory research for a better understanding and better applications. Because of the bonding characteristics of carbon atoms, the physical appearance of carbon nanotubes can often resemble rolled up chicken wire[1]. One of the interesting physical properties about carbon nanotubes is that when two different structured nanotubes are joined together , the spacing between them shows electrical behaviour, where the electronic behaviour depends on the two tubes.

Currently scientists are trying to make carbon nanotubes in large scale with a high degree of purity and less defectiveness, so that the equivalent structures will lead to the similar physical and chemical properties which ultimately make them more useful for possible nanosensors. These nanosensors could behave like semiconducting materials in microelectronic circuits to detect small changes in electric current, register chemical reactivity, in air pressure or temperature [6].

Since carbon nanotube science is relatively new, scientists from the fields of chemistry, physics and the material sciences are just beginning to unlock its mysteries and hypothesize about its potential applications.

1.2 Classification of CNTs:

According to the structure carbon nanotubes can be classified as Single wall Carbon Nanotube (SWCNT) and multi wall carbon nanotube (MWCNT). SWCNTs are considered as single sheet of graphene rolled to form seamless cylinder where as in MWCNTs a number of graphene sheets are rolled to form seamless cylinder.

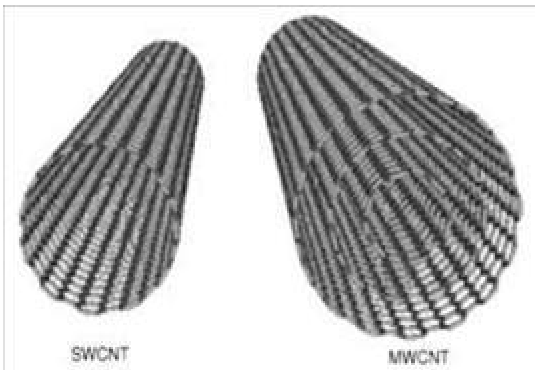


Fig5: Structure of SWCNT and MWCNT [1]

Also there are three unique geometries of carbon nanotubes which are also referred to as flavours. The three flavours are armchair, zig-zag, and chiral [e.g. zig-zag (n, 0); armchair (n, n); and chiral (n, m)]. These flavours can are classified according to the rolling of graphene sheet [1].

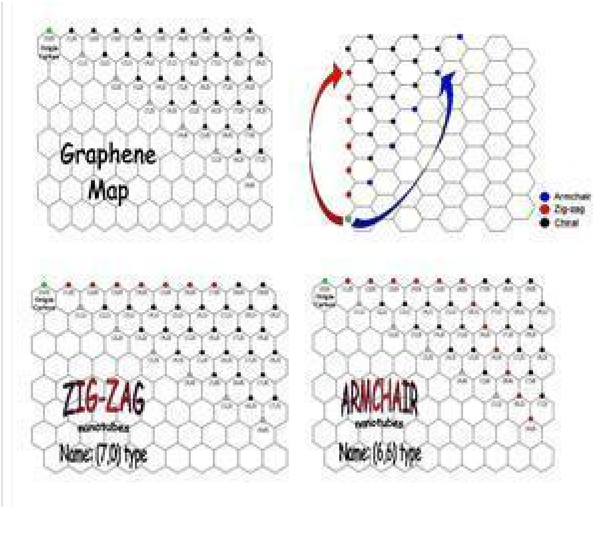


Fig6: Geometrical configuration of various CNTs [1]

[2-3]The electrical and mechanical properties are completely depend on the chirality of the nanotube and the energy band gap depends inversely on the tube diameter. As per it the armchair and zigzag act as metallic and semiconducting respectively. Theoretical studies have shown that a single-walled CNT can be either metallic or semiconducting depending on its chirality and diameter. (n, m) nanotube with n m arm- chair

are metallic for n – m integer, the nanotube are semiconducting with band gap proportional to diameter or n – m integer, the nanotubes would be quasi-semiconducting with a small band gap proportional to 1/d2. The sensitivity of electrical properties on structural parameters in unique for CNTs, which opens up numerous opportunities in nanotube systems. The diameter of the zigzag nanotube,

$d \quad a\pi \quad m^2+n^2+mn)^{1/2}$ and $V= aV_{\pi}/(3^{1/2} {}_x\, qd)$

where $a_{c\text{-}c}$ = 0.142 nm is the carbon-carbon bond length in graphene and V_{π} =0.33 eV is the Carbon π-π bond energy

1.3 Properties of CNTs[6]:

i) Strength :CNTs are strongest and stiffest materials due to the presence of strong SP^2 hybridized covalent bonding between the individual carbon atoms and hence having a high tensile strength and large elastic modulus. Under excessive tensile strain the tube undergoes a permanent plastic deformation.

ii) Hardness: The high value of bulk modulus around 546 GPa shows the superhardness of the CNTs.

iii)Kinetic properties: The striking and telescoping properties of sliding of inner tubes without friction has made it technically important to make the smallest motor in the world.

iv) Electrical properties: Metallic nanotubes having a current density of **4** 10^9 A/cm^2 which is much more than any bulk metal. Due to the nano scale cross section and large surface to volume ratio, the electron flows only along the tub axis. The conductance of CNTs is 2times the conductance in a single ballistic quantum channel. i.e $2e^2/h$. At low temperature CNTs shows reflection of induced superconductivity.

v)Optical properties: Due to the suitable electronic properties and band gap, CNTs shows good optical properties which facilitates its application in opto-electronics and photonic devices.

vi) Thermal properties: CNTs are very good thermal conductor showing ballistic conduction and having a thermal conductivity around $3500 w.m^{-1}.k^{-1}$ density. Temperature stability of CNTs is around 2000ºC in vacuum and 75ºC in air.

vii) Toxicity : Sometimes the insertion of CNTs into human body cause the cell death of the cytoplasm.

1.4 Preparation techniques of CNTs:

Present techniques have developed for the production of carbon nanotube as following

1) Arc Discharge
2) Laser ablation
3) High pressure carbon monoxide synthesis (HiPCO)
4) Flame synthesis
5) Chemical vapour deposition (CVD)
6) Pyrolysis
7) Plasma-enhanced CVD (PECVD

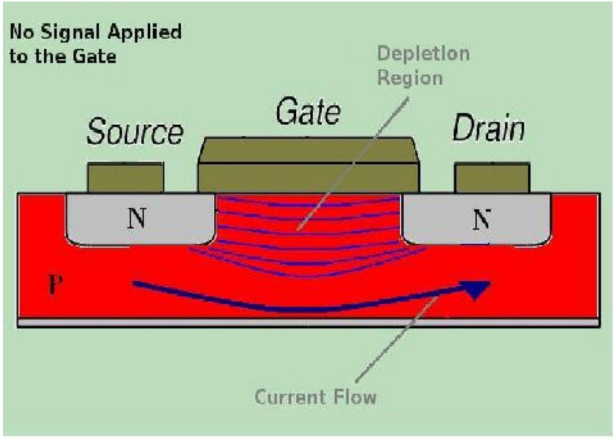
In CVD a mixture of gases passes over the hot surface undergoes chemical reaction that lead to solid deposition on the surface and the chemical compound firstly got vaporized and fragmented. The fragment or the CVD precursor diffused to the surface which is explicitly depends on the temperature and the desired species of precursor lead to a solid deposition on the substrate surface and rest of the species recombine to gas phase molecular by-products. The key factor to get high yield of pure CNTs by achieving the hydro carbon decomposition on catalyst sites and avoiding the spontaneous pyrolysis . But in CVD is being toxic and high cost effective hence less preferable for laboratory uses.

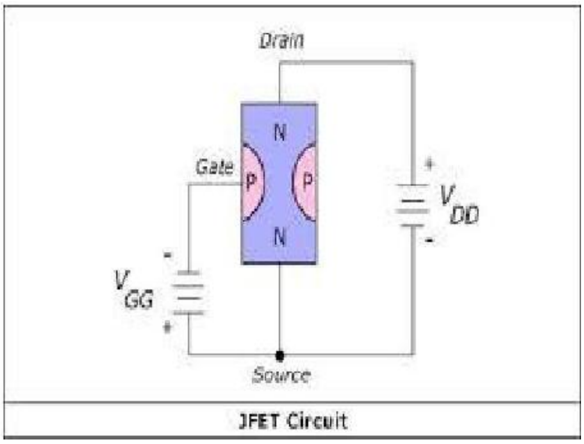
In Arc discharge process the centrifugal force caused by vibration generates turbulence and acceleration in carbon vapour perpendicular to the anode. The rotation distribution be micro discharges uniformly and generates a substrate – plasma volume and raise the plasma temperature. But this process is quite toxic, and hence harmful for rough uses in laboratory.

In LASER- ablation a continuous laser is used to vaporize the graphite target in an oven at 1200ºC. The oven filled with He and Ar gas in order to keep the pressure at 500torr. A very hot vapour plasma forms, then expands and cools rapidly. Then the catalyst begins to condense but more slowly at first and attach to the carbon clusters. But the high power requirement and cost effectiveness is less preferred.

Pyrolysis : Single step pyrolysis technique for the preparation of long aligned CNTs which is a very simple technique, low cost instrument and apparatus is required as compared to the conventional CVD or any other methods and also having low cost maintenance compared to others. In pyrolysis we just need a quartz tube to keep the mixture of catalyst and source material inside and this quartz tube is to be kept in a furnace at a pyrolysis temperature of 650ºc-900ºc such that the chemicals should lie in the reaction zone and a rubber bladder is needed to connect at one end of the tube to collect the residual gases. After the heating up to 5hrs and cooling down to the room temperature, the required substance can be prepared.

1.5 Structure and working Principle of Conventional FET :





(8) (9)

[Fig 8 and Fig9 shows the FET structure and circuit diagram[5]]

- The conventional transistors are different from the field effect transistors by their charge carriers and the input impedance.
- In transistors both the holes and electrons carry current around the junction contact but in FET either the holes or electrons acts as the charge carrier.
- Due to the reverse gate biasing the input impedance is very high in case of FET as compared to the bipolar transistors.
- Different types of FETs are 1) Junction field effect transistor
  2) Metal oxide semiconductor FET (MOSFET)
- The FET consists of a p-type or n-type channel at the middle hence respectively known as the p-type or n-type FET and doped by opposite type of semiconductor like in p-type channel the n-type semiconductor fabricated to form to p-n junctions which are called as drain and source terminal and these terminals can be inter convertible. A Gate contact is made as a common contact between the source and drain to make the four terminal device as three terminals.

Working principle:

- When the voltage V is applied between source and drain terminals and the gate terminal having zero biasing, the two p-n junctions at the sides of the bar establish depletion layers. The size of this layer determines the width of the channel and hence the current conduction through the bar.
- When a reverse voltage is applied between the gate and source terminal the depletion layer increases with decreasing the channel width and when the the depletion layer on both the sides touch each other current flow through the channel null, that means the channel goes to off state.
- It is clear from the above discussion that the current from source to drain can be controlled by the applied potential at the gate and hence
  Known as the field effect transistor .

Transfer characteristics:

1) The input characteristics can be studied by plotting the gtae voltage verses drain-source current at constant drain voltages. And the output transfer characteristics shows the plot between the drain voltage and drain current at constant gate voltages.
2) Shorted gate-drain current: it is the drain current when source short circuited to gate. And the drain voltage equal to the pinch off voltage and hence it sometimes called as the zero bias current.
3) Pinch- off voltage: it is the minimum drain source voltage where the drain current essentially becomes constant.
4) Gate- source cut off voltage – it is the gate-source voltage at which the channel is completely off state.

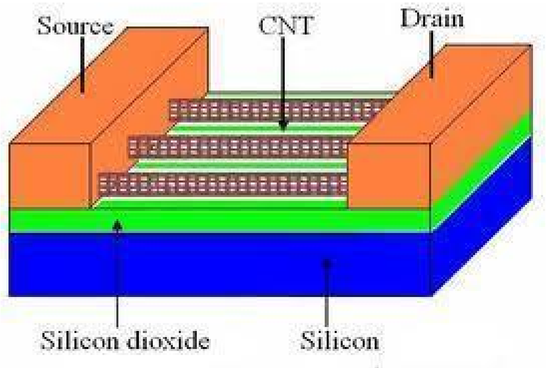
$$I_D = I_{DSS}\,(1 - V_{GS}/V_{GS(OFF)})^2$$

Advantages of JFET High input impedance allows the high degree of isolation between the input and output circuits. As the operation of FET current is independent of the bulk rather the junction contact surface and hence the noise is reduced. Due to the –ve temp coefficient of resistance, it avoids the thermal rum way. It has high power gain and high efficiency.

CNTFET: to increase the efficiency of conventional FET and for the various useful application of FET at nano level is the root interest now a days. Carbon nanotube due to its suitable electrical properties can be used as the channel in the so called FET where the carrier mobility and conduction is more than that of the normal JFET.

1.6 Advantage of CNT channel over Si channelled device:

[4] Carbon nanotube being a subject of lot many scientific research in recent years because of their small size and remarkable electronic and mechanical properties and many potential applications. Problems associated with attempting the scaling down of traditional semiconductors has led the researchers to be interested in CNT based device like CNTFET . Carbon nanotube field effect transistors are one of the most promising candidates for future nano electronics as CNTFET can be studied for a wide variety of applications like logic devices, memory devices, sensors etc. The suitable electrical properties of CNTFET can be controlled by the chirality and diameter and hollow cylinder like structure of CNT leads to a less carrier scattering through the boundaries. Due to the quasi one dimensional structure shows less phase space scattering with respect to the Si based transistor device. Forward and backward scattering is only allowed which is elastic and the long mean free path leads to quasi ballistic properties in CNT where transport occurs at long length and low field. And the strong sp2 bond makes it chemically inert allowing a large transport current. CNT can be switched with a less power than the Si based device.



[fig10 shows the structure of CNTFET[5]]

As over a past few years the critical dimensions of silicon based transistors have decreased dramatically and a few nano meter gate length have been successfully fabricated and are found to exhibit excellent electrical characteristics. As according to Moore's law the numbers of transistors in a memory cheap doubles every year and a half. This has resulted from the inter connectivity efficiency as well as from continual decrees in size.

1.2.2 Types of CNTFET:

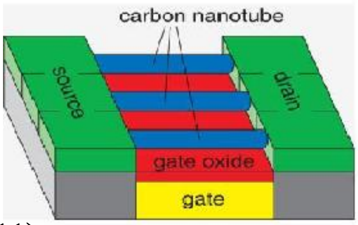
Back gated CNTFET: These are the traditional way of designing CNTFET, where the CNT is grown on the top of patterns of a prepatterned substrate.

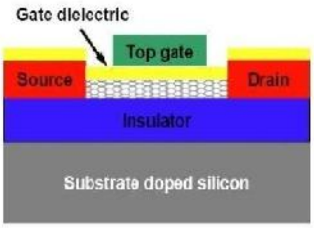
Top gated CNTFET: this is more developed technique than the previous one where firstly the

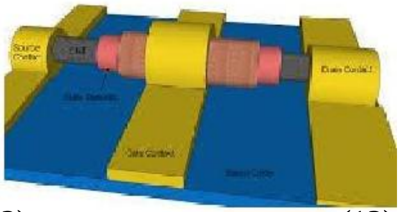
CNTs are solution deposited on the SiO2 substrate and make allocated individually by AFM and then the gate, source and drain contacts are to be made by e-beam lithography process. And then a thin top gate dielectric is deposited on the CNTs.

Wrap gated CNTFET: this is quite efficient modification of the top gated CNTFET as here leaving a small part of CNT around the metal, rest of the portion should be wrapped by a thin dielectric by atomic layer deposition. This actually reduces the gate leakage current and improves on-off ratio.

Suspended CNTFET: Suspending nanotube over a trench by catalytic process lead to a less contact between the gate and substrate cause less scattering in the CNT-substrate interface.







(11) (12) (13)

[fig11, fig 12 and fig 13 show thr back gated, top gated and wrap gated CNTFET structure Respectively[6]]

Chapter-II

2.1 Literature survey

1) P Mahanandia and K nanda et al.vol. 145, no. 3, pp. 143–148, 2008

In the paper,a simple effective pyrolysis technique has preferred to synthesize aligned arrays of multi-walled carbon nanotubes (MWCNTs) without using any carrier gas in a single-stage furnace at 700 ◦ C This technique eliminates nearly the entire complex and expensive machinery associated with other extensively used methods for preparation of CNTs such as chemical vapour deposition (CVD) and Arc plasma discharge etc. Carbon source materials such as xylene, cyclohexane, camphor, hexane, .

2) K M Lal , M J Siddiqui , Alim H et al Vol. 43, Dec. 2005, pp. 899-904.

In their work they have discussed about the fabrication of CNTFET by conventional lithography Method on the substrate and characteristic of CNTs and the metal oxide semiconductorv capacitor properties and their characteristics have been represented. They expected the performance of CNTFET will be better by improving the CNT quality and on optimizing the device structures.

3) Mostafizur Rahaman, Selvin P Thomas, S K De et al. Wiley online library 0.1002/pc.22447 According to their paper the low density polyethylene nanocomposites filled with carbon nanotubes having differnt aspect ratio have been preparedby melt mixing techniques. The effects of cnt loading , aspect ratio and frequency of electric field on electrical and dielectric properties of the nano composites have been discussed here. Dc and ac electrical resistivity are found to decrease with increase in cnt loading in the composite and the dielctric losses decreases with increases with the frequency and the electrical resistivity decrease with increae in aspect ratio.

4) Dinh Sy Hien *et al* 2009 *J. Phys.: Conf. Ser*. **187** 012060: In his work he described the fabrication of cntfet by using the cvd techniques and the source and drain contact they have done by using the conventiona llithography process.

5) Ioan Stamatina, Adina Morozana et al 10.1016/j.physe.2006.10.013 : In their work they have discussed about the production of a series of carbon nanomaterials, particularly multi-walled carbon nanotubes (MWNT), from catalytic pyrolysis of the cross-linked phenol-formaldehyde resins with different ferrocene under inert atmosphere. The morphology and structure of the samples were evaluated by TEM and XRD techniques which shows that CNTs morphology is dependent on the iron nanoparticles and their forms (Fe, Fe3C) resulted from ferrocene decomposition. The amount of nanotubes increases with iron content released from ferrocene catalyst during the pyrolysis process. Fe3C nanoparticles drive the nucleation and the growth of carbon nanotubes during the pyrolysis process.

6) Seung June Park,Min Seong Cho et al Scientific Reports 3, Article number: 3394 :

They have prepared MWNT-PMMA nanocomposites by anin-situ bulk polymerization method. During polymerization,MWNT consumed initiator (AIBN) by opening p-bonds on MWNT surfaces to make radicals. As a result, the molecular weight of PMMAs increased with the MWNT contents. FTIRspectroscopy supported the geneation of new p-bond between MWNTand PMMA.

7) Goldsmith, Matthew K. Robinson et al vol.6 5143-5149.2012:

They developed a novel detection method for osteopontin (OPN), a new biomarker for prostate cancer, by attaching a genetically engineered single chain variable fragment (scFv) protein with high binding affinity for OPN to a carbon nanotube field-effect transistor (NTFET). Chemical functionalization using diazonium salts is used to covalently attach scFv to NT-FETs, as confirmed by atomic force microscopy, while preserving the activity of the biological binding site for OPN. Electron transport measurements indicate that functionalized NT-FET may be used to detect the binding of OPN to the complementary scFv protein.

8) Shinya Aikawa, Erik Einarsson, Taiki Inoue et al 2003 *Jpn. J. Appl. Phys.* **42** 4116:

A carbon nanotube field-effect transistor (CNT-FET) is a promising candidate for future electronic devices; however, its fabrication process is still challenging. In this paper they have proposed a simple fabrication technique for CNT-FET arrays using as-grown single-walled CNTs (SWNTs) as the gate channel. In their study, a hydrophobic self-assembled monolayer (SAM) was used to restrict the catalyst-supporting area after the fabrication of an electrode array. Since it is known that droplets are trapped at rough edges of a hydrophobic surface, the deposition of a liquid-based catalyst, followed by alcohol catalytic chemical vapor deposition (ACCVD) produced SWNTs that grew only at the corners of electrode edges. The current–voltage (I–V) characterization of FETs with a 40 nm channel width showed that 98% of the fabricated devices were electrically connected and more than 50% were functional FETs (ION=IOFF > 102).

9) M F Reitag, Radosavljevic et a appl.phys.79.3326(2001)l: They have fabricated multi-walled CNT channeled FET device by passing the hydrogen gas and made the contact of copper by lithography process. They used this in a memory device.

10) Nyan-Hwa Tai a, Meng-Kao Yeh b et al carbon 44(2006) 1-9: Both theoretical analyses and experimental studies have demonstrated that carbon nanotubes (CNTs) have extremely high strength and modulus . The outstanding intrinsic mechanical properties have attracted researchers to adopt CNTs as a reinforcement for composites. Here they have discussed about the fabrication of CNTFET by using the conventional CVD technique to grow the nanotube on the substrate and the top gated CNTFET is prepared.

11) Junko Yotani *et al* 2004 *Jpn. J. Appl. Phys.* **43** L1459 :

CNTs (carbon nano tubes) have drawn much attention as a field emitter material because of the high chemical stability, superior mechanical strength, and very high aspect ratio. One can use the well-aligned CNTs produced by CVD method to fabricate the electron emitters, or can also fabricate the electron emitters by a screen-printing method, which is very easy for mass production. In this study, CNTs were screen-printed on the ITO/glass substrate, and were irradiated by an UV (ultra-violet) laser in order to improve the emission behavior of the emitter by cleaning the top surface of screen-printed CNTs or by inducing defect sites.

12) Yongsun Kim *et al* 2007 *Nanotechnology* **18** 475712: They have fabricated a CNT channeled device having both local and global gate and studied the current- voltage curve where the trans conductance of the CNT-gate is found to be 20 times that of the transconductance in local gate-substrate interface.

Objectives of my Project:

- From literature survey, I found people have prepared CNTs by using the high cost equipments like CVD, PECVD etc and somehow the toxic techniques like Arc discharge, which is quite harmful for lab uses and hence I have chosen the simple one step pyrolysis technique to prepare long aligned CNTs which doesn't need any high cost apparatus and and easy to handle for laboratory uses with reference to P Mahanandia and K nanda et al.vol. 145, no. 3, pp. 143–148, 2008.

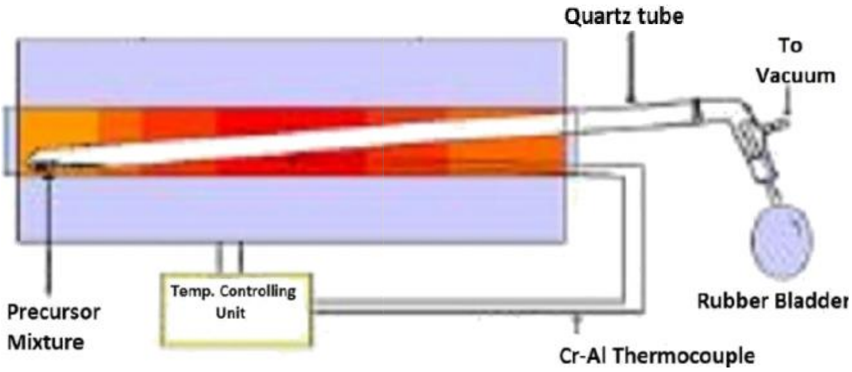
➢ According to the suitable electrical and mechanical properties of CNTs, researchers has de-veloped the CNTFET device by using the CVD,PECVD etc for the growth of nanotube on the substrate and contacts are made by the cost effective techniques like Atomic layer deposition or e-beam lithography and hence I decided to fabricate a device analogues with the FET structure, in fact similar configuration of CNTFET to study the current-voltage characteristics and the change in slope when it is exposed to various external factors like water va-pour or LASER etc.

Chapter -III

Experimental Details

[3.1.1 Preparation of CNTs by Pyrolysis technique :

CVD and PECVD are the most common techniques for synthesis and preparation of long aligned CNTs.



[Fig9 shows the pyrolysis system[7]]

The simple apparatus requirement , low maintenance and low cost effectiveness and easy availability of the pyrolysis system make it preferable for the lab uses. We have prepared the carbon nanotube by using this technique.

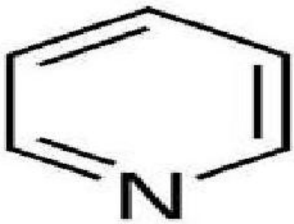
2.1.2 Materials and Methods :

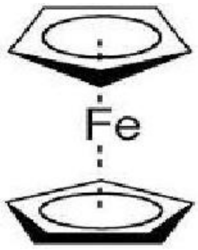
Required chemicals : acetone,ferrocene, pyridene

Before going to the procedure let's discuss about the chemicals we are taking for the purpose of preparation.

- Pyridene: **(C_5H_5N))-** It is an organic compound which is completely soluble in water,alcohol,ether and benzene. The structural formula is similar to benzene one methyl Group is replaced by by nitrogen. This is a colourless liquid with an unpleasant smell.

- Ferrocene(**Fe (C_5H_5)$_2$)**: this is a good catalyst with a structure consists of an iron atom is sandwitched between two carbon rings.





Procedure:

The quartz tube should be cleaned properly with the acetone to avoid any undesirable contamination in the reaction and the source and catalyst to be taken should be weighed properly. After proper weighing, the mixture of 18mg of catalyst ferrocene and 2ml of carbon source material was taken in a quartz tube of diameter 1cm and length 70cm, with its one end closed and the other end of the quartz tube is connected with a rubber bladder to collect the residual reacted gases. The whole assembly is placed inside the furnace and heated upto a pyrolysis temperature of 850ºC to activate the reaction between the source and catalyst inside the reaction zone. The reaction is continued for 5 hrs and then cooled downed to room temperature for 1day . At room temperature the reaction quartz tube is taken in to the safety removal of the rubber bladder. Then after cooling for a long time the black powder like substance inside the quartz tube was collected by using a thin rod, which is cleaned properly to remove the contamination. Then the prepared sample is verified by the different characterization studies like field emission scannig electron microscope study and XRD study etc.

3.2. Fabrication of CNTFET configured device:

>> As discussed in chapter-I, FET is the 3 terminal device having a gate electrode common in between the source and drain.. The fabrication of FET can be done by doping a p-type or an n-type semiconductor by its corresponding opposite type of semiconductor to get two p-n junctions, where one end is constituted with a metal contact called source and another one is drain and both these terminals are inter convertible. A gate dielectric is needed to remove the leakage current between the substrate and contact interface. Generally SiO_2 is used for this purpose. But in my project I have tried to fabricate a device equivalent to the CNTFET, where the CNT we are using as the channel for conduction, is of millimetre length multi walled metallic nanotube.

3.2.1 Substrate and dielectric selection[6]:

SiO_2 is a suitable dielectric for the use in conventional FET due to the following properties

- Atomic weight of 60.08 amu
- Thermal conductivity 0.014 w/cm.k
- Thermal diffusibility 0.006 cm^2/sec
- Relative dielectric constant of 3.9
- Refractive index 1.46
- Break down field 6 $_x$ 0^8 v/m
- Atomic density $2.27*10^{22}$ mol/cm3
- 9. Energy gap~9eV
- 10. Melting point 1700ºC
- 11. Electron affinity 1ev

The above properties of SiO_2 makes it suitable gate dielectric for FET fabrication purpose.

We are using the Si semiconductor substrate for fabrication of FET as Si is a semiconductor with a band gap of 1ev.

3.2.2 Procedure

The semiconducting n-type silicon substrate is first cleaned properly with the acetone and sonicated for 15min in acetone to avoid the contamination. Then the Si substrate is dried for some time in the decicator to be in vacuum. The dried Si substrate is put in the furnace at temperature of 850°C to grow an oxide layer on the surface of Si at one side, keeeping the other side as conducting.

After an annealing process of 5hrs the substrate is cooled to room temperature for one day.

The resistance was checked by using the multimeter to verify the oxidaton of one side of the Si and the conducting surface of Si substrate. Hence we got a thin layer of SiO_2 on the n type Si substrate. Then the substrate- dielectric plate is again cleaned properly by acetone and sonicated by acetone for 15min for removal of contamination. For a trial to get the contact pattern on the surface, I used the teflon masking for gold coating on Si-surface as teflon can resist the high temperature due to its high melting point and this is done succesfully and the resistance and I~V measurement was done by multimeter and source meter respectively.

For the fabrication purpose of CNTFET , firstly a bundle of CNT with mm length, characterized by FESEM and XRD, simply kept on the SiO_2 surface and lubricated by methanol to stick to the surface without a break in bundle structure. Then the CNT - substrate is heated by the lamp and left to be dried for one day. After the drying process the silver paste is used to touch the both edges of long CNT for the purpose of making drain and source contact analogues to a FET. Then the silver paste contact with the CNT is left to be etched for 1 day to dry properly and the insulating copper wires are made prepared by scrubbing at both the ends to remove the insulation coating for the purpose to make contact wires of drain and source. Then the copper wire is connected at the source and drain ends by the conducting silver paste. And the whole system again dried for 1day to get ready for measurement circuit. Firstly the I~V characteristics is studied without the gate contact, where we got linear variation of voltage with the current. Then the gate contact is made at the opposite conducting side of the substrate and left to be dried for making the contact strong and connected by a conducting copper wire. The fabricated CNTFET having a channel length of 500micron, verified from the FESEM and the gate length is measured around 1mm and the device length is around 3mm.

Then the device is ready for the measurement of the current-voltage characterization .

Fig 3.2 : CNTFET device

Chapter-IV

Characterization Techniques

The following characterization techniques were used to study the structural, morphological and electrical properties of long-aligned CNTs.

4.1 X-Ray Diffraction (XRD)

The physical properties of CNTs greatly depend on the direction of chiral vector during the rolling of graphene sheet, the tube and length diameter, aspect ratio (ratio between diameter and length of CNT) and the nanotube morphology. X-ray methods offer structural information at different length scales from the single nanotube to the nanotube bundle.

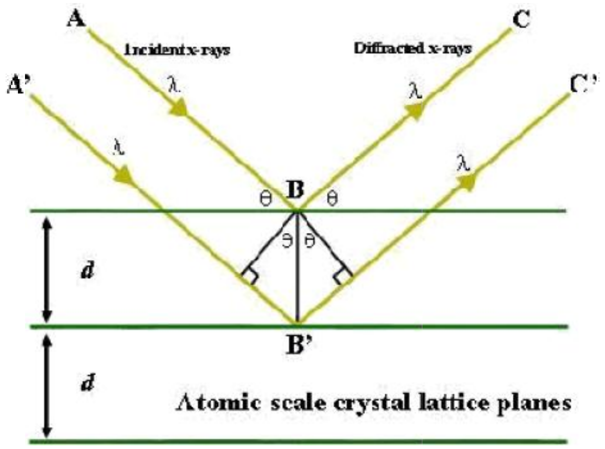


Fig. 4.1 X-Ray phenomena[6]

X-Rays are electromagnetic radiation, used for phase identification of a crystalline material and can provide information on a unit cell dimension. XRD is based on constructive interference of the monochromatic X-Ray and crystalline sample when the condition satisfies Bragg's law

$$N \lambda = 2d \sin \theta$$

The diffracted x-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angle all possible diffraction direction of the lattice should be attained due to random orientation of powder crystal. Conversion of diffraction peak to d-spacing allows identification of a mineral because mineral has a set of unique d-spacing.

The crystallite size can be calculated by using the shearer formula

$$D = 0.91\, \Lambda / B\cos\theta$$

where Λ=wavelength of the X-RAY source

B= full width at half maxima of the peak

4.2 Field Emission Scanning Electron Microscope (FE-SEM)

A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. In SEM, a beam of highly energetic electrons strike the sample and extracts the secondary electron, back scattered electrons from the sample surface. The electron beam interaction with the atoms make up the sample for production of signals to be collected at the detector system. This signal contains information about the samples surface, composition, topography and electrical conductivity.

FE-SEM uses field emission gun producing a cleaner image, less electrostatic distortions and spatial resolution less than 2 nm (that means 3 or 6 times better than SEM).

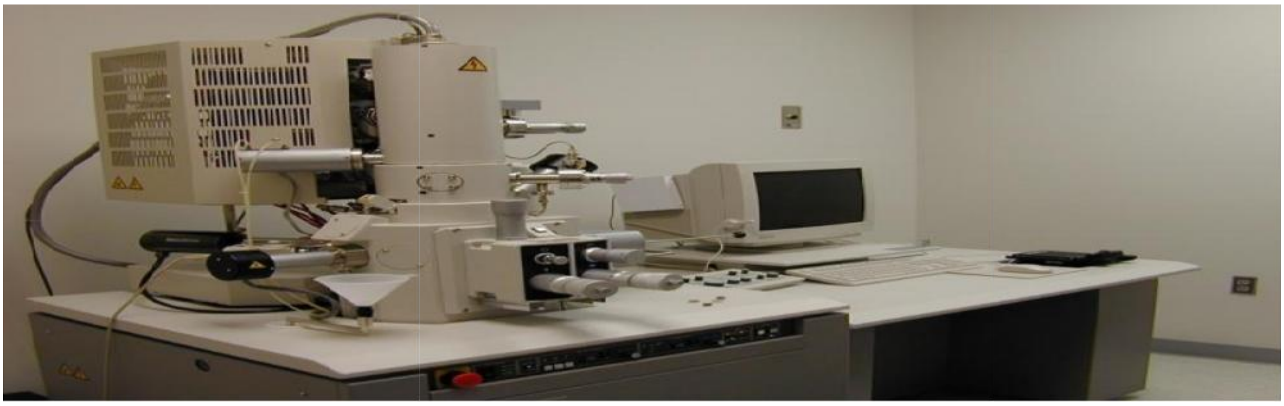


Fig. 4.2 Field Emission Scanning Electron Microscope[6]

4.3 I~V characterization:

we generally use the source meter or semiconductor parameter analyser for current- voltage measurement purpose. This source meter is a four probe arrangement with inner two probes for voltage and the outer probes for

Current measurement. From the i~v study of a sample we can find out the electrical properties like the conductivity, resistivity, transfer characteristics and the energy band gap also can be found.

Fig 4.3 source meter[6]

Chapter-V

5.1Results and Discussion:

5.1.1 XRD Analysis :

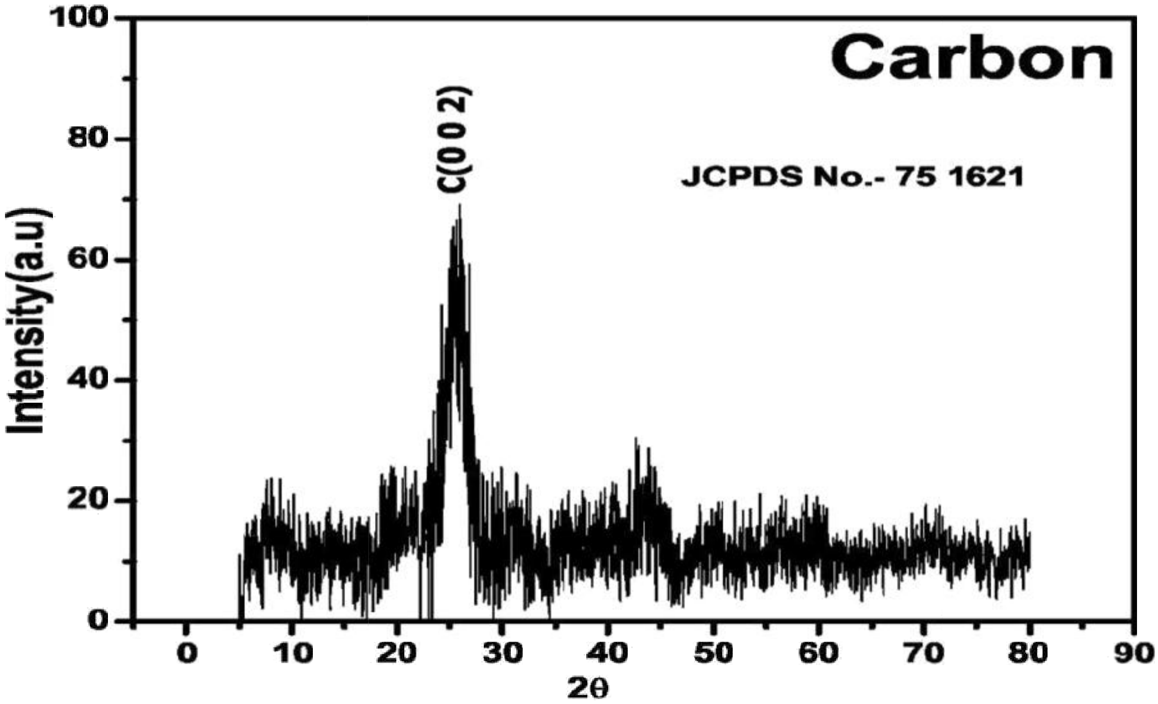


Fig 5.1.1 XRD Peak of CNT bundles

XRD is the most important tool to study the crystal phase and the crystal structure of the sample element. The typical XRD pattern of CNT as shown in figure , which is confirmed after comparing with the international centre for diffraction data(ICDD), reveals a peak at 2Θ angle of 26º The plane of diffraction is found at (0 0 2) observed from the graphitic peak of carbon. And the iron peak is observed showing the presence of catalyst ferrocene. The background noise of the XRD shown in the above figure due to the presence of catalyst and the impurities during scanning of sample surface.

5.1.2 FESEM Analysis of The CNT channel:

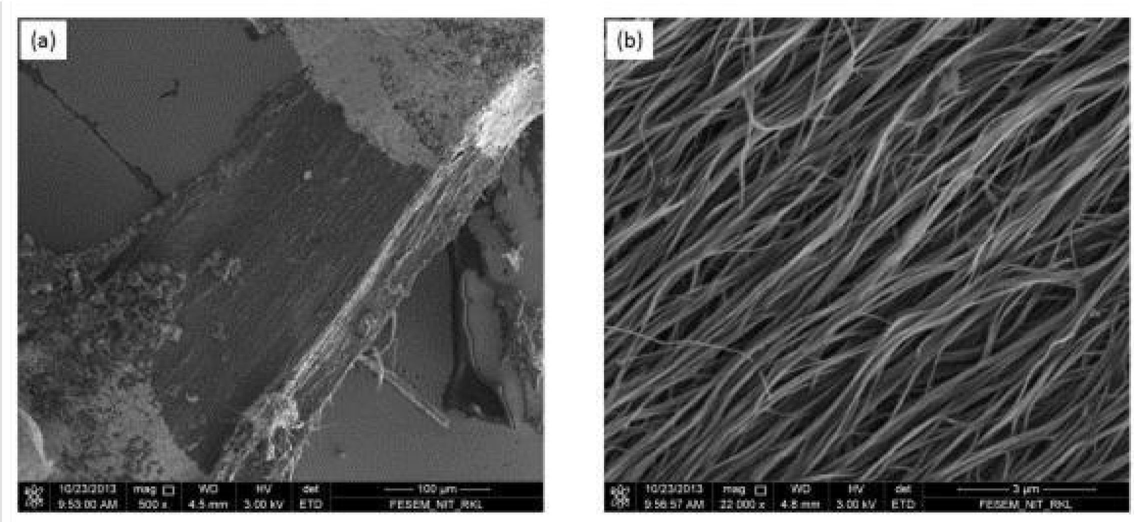


Fig 5.2 [SEM image of the carbon nanotube shown in **fig 5.2 and fig 5.3**]

The FESEM image of as prepared carbon nanotube by pyrolysis method shows nanotube structure of length around 10 micrometer and closed at one end due to the growth on the catalyst surface. And the images show that some of the tubes are entangled and some are aligned as per their growth mechanism. Some plums like structures around the bundles of CNTs reveals the presence of either the catalyst or the impurities during the experiment.

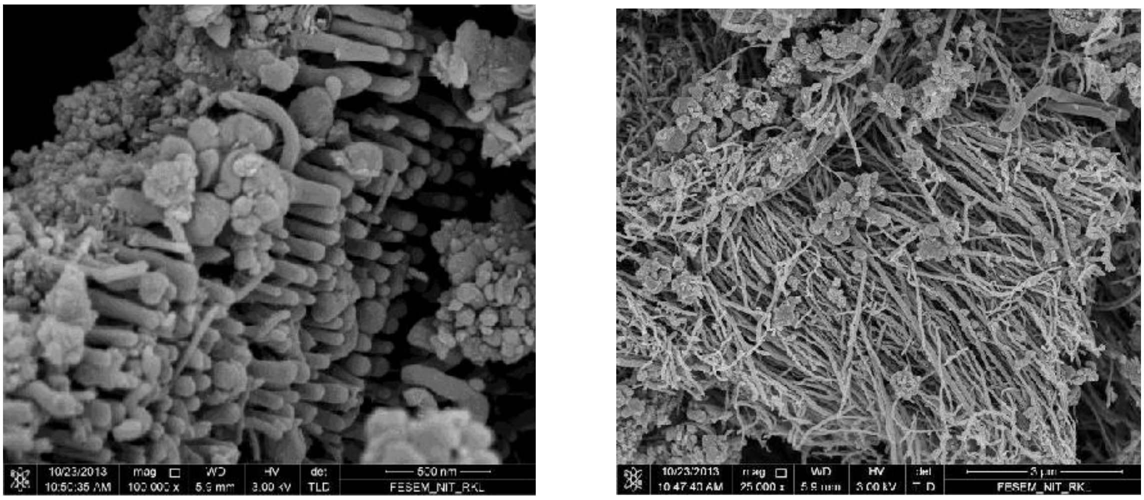


Fig 5.3 : FESEM image of CNTs

The above FESEM image shows that the CNT prepared by pyrolysis technique having a length of 6micron and the background reveals the presence of impurities and the catalyst. The closed tip in the figure informs us about the growth of CNTs on the catalyst surface.

5.1.3 TEM Analysis of the CNT channel :

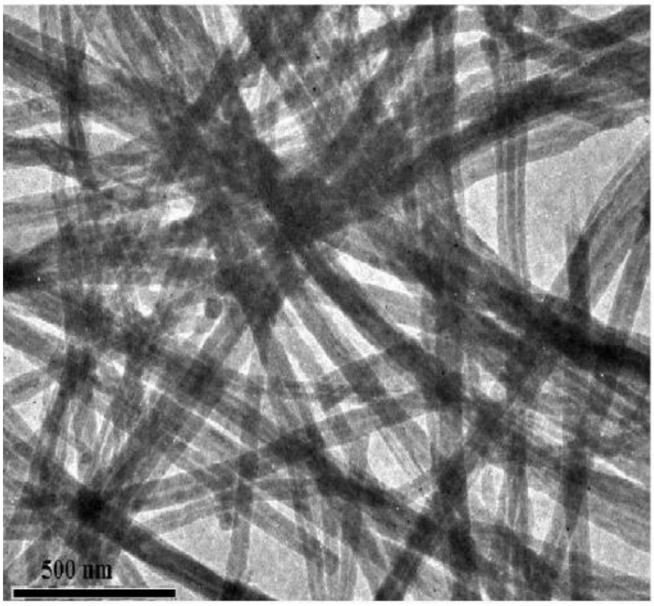


Fig 5.3.1

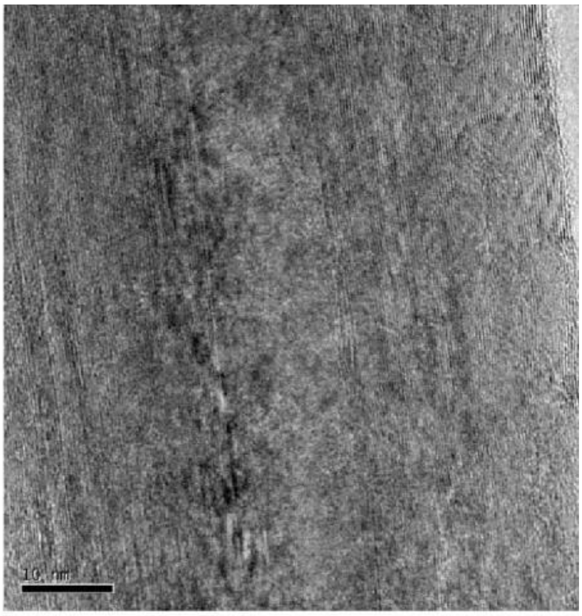
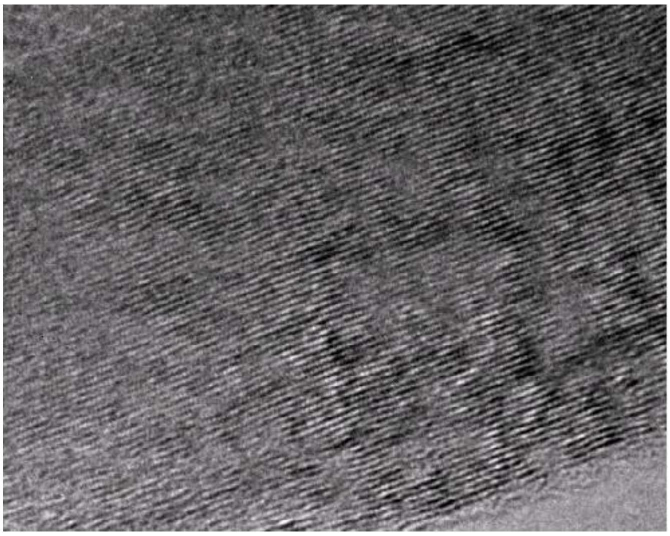


fig 5.3.2

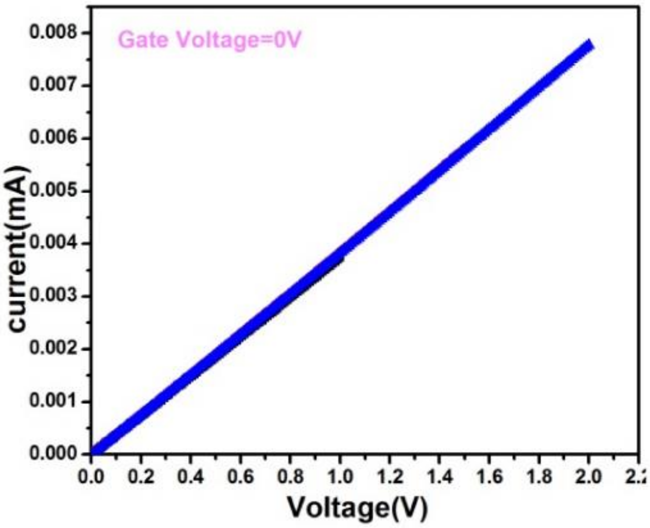


fig

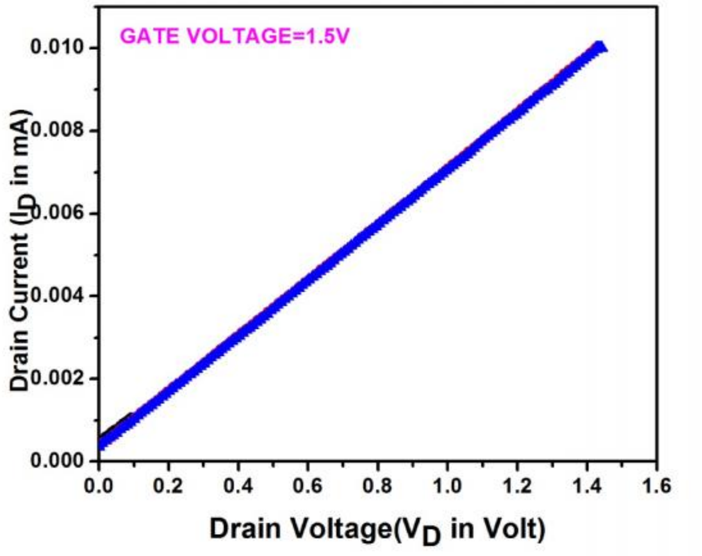
[fig 5.3.1, 5.3.2 and 5.3.3 is showing the TEM images of CNTs]

The TEM images from the above figures reveals the highly crystalline structure of the CNTs and the multi walled nanotube structure is verified and the diameter of the nano tube is found to be 75nm from the TEM image.

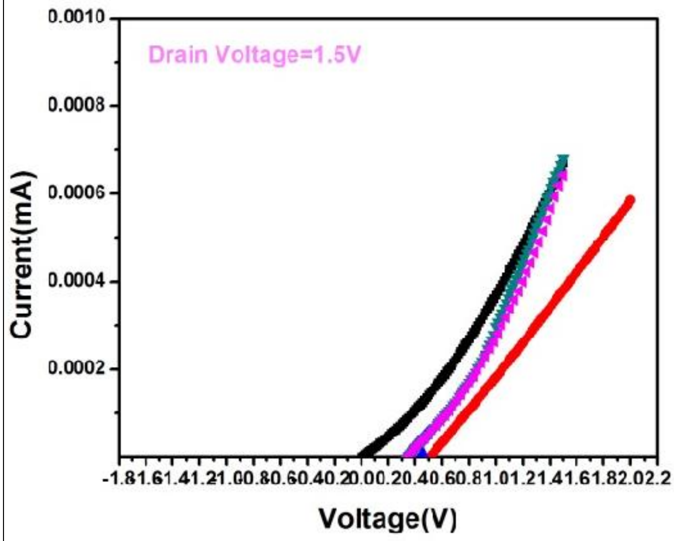
5.1.4 Current- Voltage Characterization :



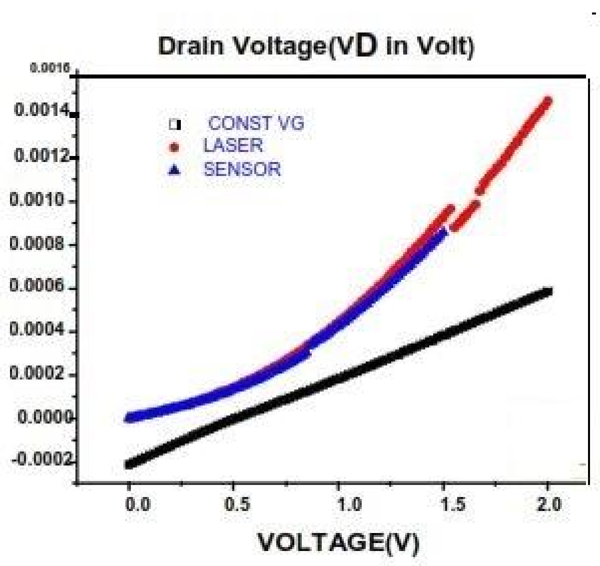
(a)



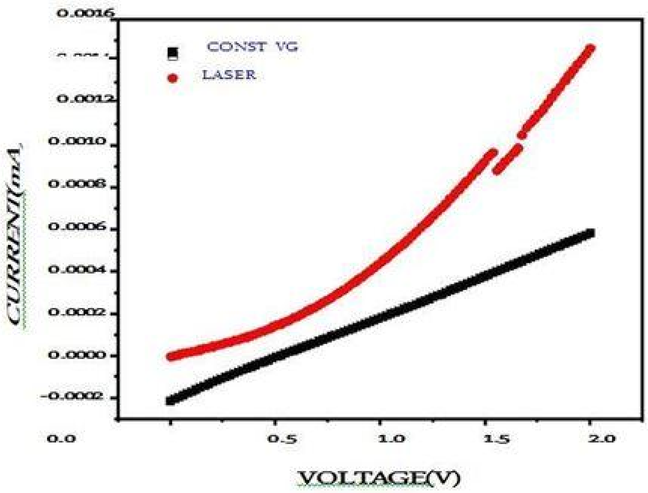
(b)



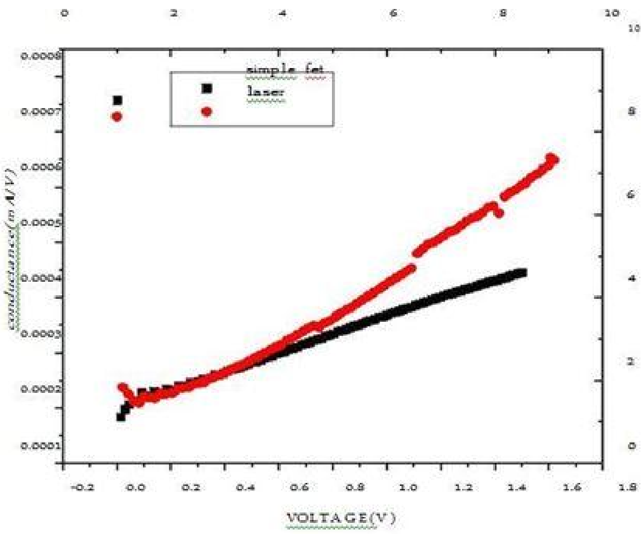
(c)



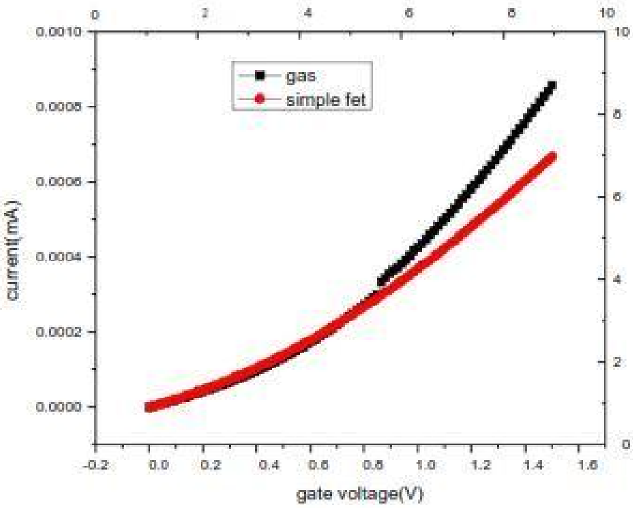
(d)



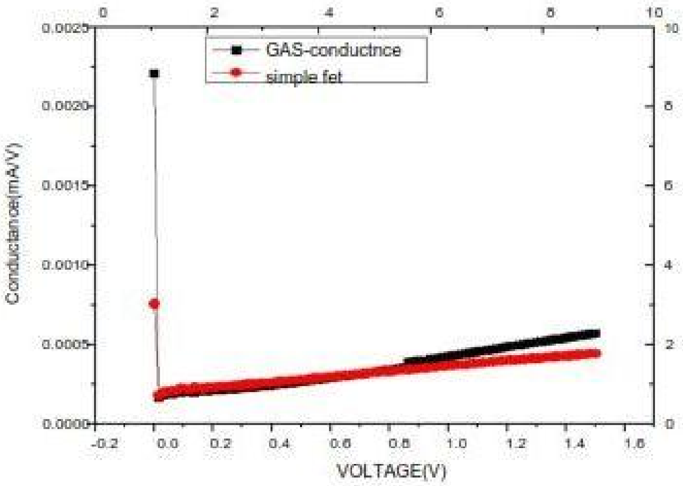
(e)



(f)



(g)



(h)

The current ~ voltage plot in fig (a) and fig(b) at a zero gate voltage and 1.5V respectively showing a straight line curve which reveals the metallic transport in CNT with a high conduction probability. The metallic transport cause a high conductance with less scattering and a large scale flow with the application of a low biasing. But when we are exposing the device to water vapour , due to the absorption which leads to a carrier scattering showing a little difference in the resistance or the slope of the I~V curve. The increase in conductance in case of laser exposure showing a change in the carrier mobility of the CNT channel as the change in the drift velocity of the carrier electrons on the surface of the nanotube which can be concluded from the change in slope of I~V curve .

When the gate terminal is provided by a constant supply of 1.5V, the output transfer characteristics is plotted by taking the drain –source voltage in X-axis and the drain current in Y- axis, showing a straight line curve with a little shift in current axis due to the substrate induced biasing in the schotky contact. Fig (c) is the plot between the gate voltage and drain current with respect to the application of a constant drain voltage and looking at the current flow around the schotky contact interface of the gate and the silicon semiconducting substrate. Fig(f) and fig(h) represents the conductance and voltage variation of the device to reveal the change in conductance due to the exposure to the water vapour and LASER light. From the rough calculation of the raw data shows the change in conductance value is observed as 2625 ohm^{-1}, 2633ohm^{-1} a change in conductance value with the application of LASER and vapour respectively, which is more than that of the previous case.

The constantly increasing region of I~V curve reveals the high conductivity of the CNT nano channel. Due to the application of laser beam more number of electrons from the valence band will excite to the conduction band, that means the Fermi level shifting is occurring which is revealed from the graph where the slope of this laser sensing graph is more than that of the original I~V plot where we are measuring the drain current and gate voltage at a constant drain-source voltage. i.e the resistance is decreasing in this case.

5.2 Conclusion :

We have successfully prepared few micron length CNTs analyzed from the FESEM, and XRD study showing a semi metalic behaviour. The CNT ,we are using as the channel in the fabricated CNTFET configured device, is prepared by Prof. Mahanadia, is having millimetre length and shows a multi walled metallic behaviour which can be verified from the electrical transport characteristics with a substrate induced biasing. The change in slope of the I~V curve reveals the surface reactiveness of CNTs towards the foreign molecules. The LASER sensing is used to check the sensitivity of CNTs showing a change in the resistance and conductance values. Hence the use of reduced length channel in a FET correlated device can lead it to a better efficiency to intact with the various potential applications has verified in a small angle from the above discussion.

Future work:

- The modification of this project to get a better measurement, we can use the semiconducting long single walled CNTs and an uniform magnetic field exposure can be studied to find out the change in carrier mobility of the surface electrons of SWNT which will guide us to move forward for the further potential application of CNTs.
- Instead of tubular structured CNT, we can use the planner Graphene sheet with a perfect contact by advanced techniques to study the transfer properties and the change in surface sensitivity with exposure to various external factors.

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